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Halogenated Hydrocarbons and Their Mixtures: A Decade of Progress in Calorimetry

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Physical and Chemical Properties Division

Chemical Science and Technology Laboratory

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CONTENTS

1. Introduction.....	2
1.1 Objective.....	2
1.2 Scope.....	2
1.3 Organization.....	2
2. Heat Capacity Calorimetry.....	2
2.1 Heat Capacity Measurements of Pure Halogenated Hydrocarbons.....	3
2.2 Heat Capacity Measurements of Mixed Halogenated Hydrocarbons.....	6
3. Density.....	7
3.1 Density Measurements of Pure Halogenated Hydrocarbons.....	7
3.2 Density Measurements of Mixed Halogenated Hydrocarbons.....	7
4. Vapor Pressure.....	7
5. Impacts of this Program.....	9
6. Conclusions.....	10
7. References.....	10

LIST OF TABLES

Table 1. Ranges of temperatures, pressures, and number N of data for heat capacity C_v measurements on halocarbons at NIST.....	15
Table 2. Ranges of temperatures, pressures, and number N of data for saturated liquid heat capacity C_σ measurements on halocarbons at NIST.....	16
Table 3. Mole fraction compositions and ranges of temperatures, pressures, and number N of data for heat capacity C_v measurements on halocarbon mixtures at NIST.....	17
Table 4. Ranges of temperatures, pressures, densities, and number N of data for p- ρ -T measurements on halocarbons at NIST.....	18
Table 5. Range of temperatures and number N of data for saturated liquid densities of halocarbons at NIST.....	19
Table 6. Mole fractions and ranges of temperature, pressure, density, and number N of data for p- ρ -T measurements on halocarbon mixtures at NIST.....	20
Table 7. Ranges of temperatures, pressures, and number N of data for vapor pressures of halocarbons that are directly measured, calculated from saturated liquid heat capacity C_σ and calculated from two-phase internal energy increments $U^{(2)}$ at NIST.....	21

HALOGENATED HYDROCARBONS AND THEIR MIXTURES: A DECADE OF PROGRESS IN CALORIMETRY

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An accurate knowledge of thermodynamic properties is a prerequisite to design efficient and cost-effective refrigeration systems that use halogenated hydrocarbons as working fluids. We present a review of a long-range NIST project concerning experimental methods and measurements of thermodynamic properties. In total, more than 6000 measurements were reported on selected pure components and their mixtures. Key properties measured include vapor pressures or vapor-liquid equilibrium, densities, and heat capacities. Because of their significance, the review emphasizes calorimetric measurements of heat capacities at constant volume C_v by means of an adiabatic method, while it also covers a concurrent effort that produced vapor pressures and densities. This measurement program produced thermodynamic measurements for pure halogenated hydrocarbons including HCFC-13, HFC-23, HFC-32, HFC-41, HCFC-123, HCFC-124, HFC-125, HFC-134a, HFC-143a, and HFC-152a, and for their binary and ternary mixtures including HFC-32+HFC-125, HFC-32+HFC-134a, HFC-125+HFC-134a, HFC-125+HFC-143a, and HFC-32+HFC-125+HFC-134a. In addition to heat capacities, calorimetric studies produced the first reliable measurements of triple point temperatures and enthalpies of fusion for seven pure compounds. Also, heat capacities measured in the two-phase region have provided a useful means for calculating thermodynamically consistent vapor pressures at temperatures between the triple-point and the normal boiling-point temperatures. Taken as a whole, this body of calorimetric measurements had a significant impact on the development of accurate predictive models. Because of the sensitivity of the mathematical models to the behavior of the heat capacity, the heat capacities from this project have strongly influenced the selection, by an international panel, of the most reliable equations of state for HFC-32, HCFC-123, HFC-125, HFC-134a, HFC-143a, and HFC-152a. The heat capacities measured for mixture systems have had an equally strong impact on the development of accurate models of mixtures.

Key words: calorimetric property; density; halogenated hydrocarbon; heat capacity; mixture; vapor pressure

1. Introduction

1.1 Objective

Among the long-range objectives of research in thermophysical properties at the National Institute of Standards and Technology (NIST) is the development of accurate predictive methods for calculating the properties of gaseous and liquid mixtures of halogenated hydrocarbons (halocarbons). These models play a key role in design of refrigerating equipment and optimization of materials and energy usage. The ongoing development and testing of these models relies heavily on benchmark experimental measurements. The purpose of this review and bibliography is to provide design engineers, data analysts, and experimentalists with a compilation of the calorimetric and densimetric studies of halogenated hydrocarbons by the Experimental Properties of Fluids Group during the decade from 1992 to 2001.

1.2 Scope

In the last 10 years, considerable progress [1,2] has been made in the measurement of thermophysical properties of halocarbons and their mixtures. A knowledge of thermophysical properties is essential when a detailed analysis of performance of refrigeration cycles is needed. Both thermodynamic and transport properties are required. In the present work, we will focus primarily on a key thermodynamic property, heat capacity, but will also discuss the closely related topics of density and vapor pressure.

1.3 Organization

The bibliography is arranged in three sections by thermodynamic property. The discussion is followed by seven tables that present the substance designation, the compositions, the temperature range, the pressure range, the number of points and the reference numbers. A discussion is provided on some impacts of this research program.

2. Heat Capacity Calorimetry

Heat capacities are fundamental to our knowledge of the thermal properties of any substance or mixture. They may be regarded as a measure of the rate of change of energy storage in molecular systems. Heat capacity is defined by the path taken during an exchange of energy with the surroundings; the path may be at a constant pressure, at constant density, or

along a phase saturation curve. In practice, we may measure a change in enthalpy at constant pressure C_p or a change in internal energy at constant volume C_v . However, it is not possible to measure a heat capacity at a fixed pressure condition of vapor-liquid saturation. This is so because an addition of a small quantity of energy will evaporate a portion of the sample but will not raise its temperature, and thus an infinite heat capacity would be calculated. On the other hand, it is feasible to directly measure heat capacity in the vapor-liquid two-phase region $C_v^{(2)}$ and then calculate the saturated liquid heat capacity from well-established thermodynamic relations.

Since 1961, the NIST laboratories have been measuring heat capacity at constant volume C_v for liquids, compressed gases, and liquids in coexistence with gases. This work was initiated to fulfill the needs of the National Aeronautics and Space Administration (NASA) to accurately determine the thermodynamic properties of the cryogenic rocket propellant hydrogen and of oxygen. In connection with this work, Goodwin [3] described a constant volume adiabatic calorimeter for the study of heat capacities of compressed gaseous and liquid hydrogen [4] at very low temperatures. Three decades later, Magee [5] described modifications and automation of this calorimeter in addition to new C_v measurements for compressed gaseous and liquid nitrogen. More recently, Magee and colleagues [6] developed a high temperature constant volume adiabatic calorimeter and acquired new C_v data for water. This new calorimeter is a fully automated device that uses twin calorimetric bombs to minimize effects of corrections for parasitic heat losses to the surroundings.

2.1 Heat Capacity Measurements of Pure Halogenated Hydrocarbons

McLinden [2] has described the genesis of a major NIST program, which had its beginnings in 1909 and a resurgence in the 1980s, to measure and correlate the properties of refrigerants, including both natural and synthetic substances. In the 1980s, mounting evidence that implicated chlorofluorocarbons in stratospheric ozone depletion was the impetus [7] for a new program on the properties of alternative refrigerants. The early studies resulted in a seminal paper [8] by 12 authors who formulated the thermodynamic properties of HCFC-123 and HFC-134a with a 32-coefficient equation of state fitted to measurements of the critical point, vapor pressures, saturated liquid and vapor volumes, superheated pressure-volume-temperature behavior, second virial coefficients, and a correlation for the heat capacity of the ideal gas. In

1989, no liquid heat capacities were available for its formulation. Notwithstanding this fact, HFC-134a was widely considered to be among the *best characterized substances* in the world, and in a category with H₂O, since the available measurements had been made with state-of-the-art methods over wide ranges of conditions. Since our prior experience with hydrocarbons had shown that heat capacities provided essential information for the temperature derivatives of an equation of state, it was necessary to measure them for the development of accurate equations of state for refrigerants. Later that same year, measurements of liquid-phase C_v were initiated for HFC-134a and were immediately compared with calculations from the equation of state formulation in Ref. [8]. While it was not a revelation that measurements and models did not agree within the experimental uncertainty of 0.5 %, the actual size of the discrepancy far exceeded any reasonable expectations. In fact, the measured liquid phase heat capacities were as much as 60 % higher than the calculated values. From this point onward, C_v measurements were a mandatory part of our characterization of other alternative refrigerants. After the initial study, heat capacity measurements were reported [9] for the saturated and compressed liquid phases of HFC-134a at temperatures from 172 to 343 K and pressures up to 35 MPa, with comparisons to both a newer equation of state [10] and published experimental heat capacities [11] at constant pressure (after conversion to C_v) from Keio University. The observed agreement was within 0.5 %, which is less than our experimental uncertainty. In addition, the first measurement for the triple point temperature (169.85 ± 0.01 K) of HFC-134a was reported, and the following derivatives,

$$\left(\partial U^{(2)} / \partial V\right)_T = T \left(\frac{dp}{dT} \right)_\sigma - p_\sigma \quad (1)$$

$$\left(\partial C_v^{(2)} / \partial V\right)_T = T \left(\frac{d^2 p}{dT^2} \right)_\sigma \quad (2)$$

were used to examine the internal consistency of the two-phase heat capacities. This consistency check is possible because the two-phase heat capacity at constant volume $C_v^{(2)}$ must obey a linear relationship in volume. Equation 2 suggests that the second temperature derivative of the vapor

pressure can be calculated from the slope of each isotherm in Figure 2 of Ref. [9], which also shows that the measurements of two-phase heat capacities are internally consistent to within 0.2 %.

Our early experimentation with halocarbons taught several important lessons to carry forward into further studies:

(1) Never take for granted a supplier's purity statement. Before the first measurement, verify content of impurities by gas chromatography-mass spectrometry or oxygen electrochemical analysis, and collect a sample to test after the runs to check for thermal-decomposition reactions. Decomposition may be catalytically enhanced by metals (including silver and copper) at temperatures as low as 410 K. Since halocarbons are hygroscopic, all samples contain at least some water and must be dried over an activated molecular sieve. Check for water content after the experiments are completed. After one experiment, this check revealed that 500 ppm water had been picked up from the walls of a pressurization system. The experiment in question had to be repeated after those volumes were dried by flowing hot dry nitrogen gas through them for 2 h. Many samples are saturated with air, and should be degassed by distillation or by freezing and pumping, followed by an oxygen analysis with an electrochemical oxygen analyzer.

(2) A large enthalpy of vaporization can cause the sample temperature to drop quickly, even to below its triple-point temperature, causing complete blockage of the discharge capillary; in these cases, one must heat the cell and connecting capillary for up to several hours to melt the plug, due to a relatively large enthalpy of fusion. Another potential hazard caused by blockage is that one cannot monitor the pressure inside the cell during the heating step, so great care must be exercised to not substantially raise the temperature of the cell.

(3) Few accurate measurements of heat capacity exist, especially for mixtures or for liquids at temperatures below ambient. Before the measurements are initiated, a preliminary equation of state should be used to calculate the pressure-volume-temperature conditions in the regions to be explored. Closely spaced measurements produce a T - p - C_v surface with sufficient detail to test equation of state calculations. And finally, repeat each run at least once to check consistency before moving to the next run.

McLinden and Watanabe [1] have described an international cooperative arrangement that was organized in 1990 under the auspices of the International Energy Agency. Referred to

as *Annex 18 - Thermophysical Properties of the Environmentally Acceptable Refrigerants*, this activity sparked worldwide interest in the properties of halocarbons. During the 1990s, Annex 18 provided considerable influence to sustain and expand interest in an experimental measurement program at NIST that encompassed studies on HCFC-123, HFC-134a, HFC-32, HFC-125, and HFC-143a, and on binary and ternary mixtures containing HFC-32, HFC-125, and HFC-134a. Table 1 presents the ranges of conditions studied for heat capacities C_v of the research under Annex-18 on HFCs and HCFCs plus five other halocarbons. Table 2 presents the ranges studied for two-phase heat capacities and saturated liquid heat capacities for the same list of halocarbons.

2.2 Heat Capacity Measurements of Mixed Halogenated Hydrocarbons

Reliable heat capacity measurements at constant volume for mixtures are among the most scarce thermodynamic properties. In addition to the usual care taken to measure the primary variables of the experiment, one must prepare and handle mixtures with attention to additional details. It is essential to begin with high purity ingredients for which the purities were confirmed by chemical analysis. One must use a gravimetric method with a high precision balance to prepare mixtures. With this in mind, the impurities present in the ingredients are the single most important source of uncertainty that propagates to the final results. In addition, thermal mixing was necessary to achieve blending of the ingredients and prevent de-mixing before their use. For thermal mixing, the bottom of the gas mixture bottle was heated to a temperature 40 °C higher than the top for a period of two weeks before the mixture was used for measurements. Table 3 presents the ranges of conditions studied for heat capacities C_v of binary and ternary mixtures of halocarbons. These heat capacities provide an excellent means to check the predictive ability of mixture models for derived properties. Lemmon and Jacobsen [20] have reported a mixture model explicit in Helmholtz energy and that uses independent variables of density, temperature, and composition. The primary data that was used to fit the adjustable parameters in the model are mixture densities. The mixture Helmholtz energy formulation was then used to predict heat capacities. For the first entry in Table 3, an equimolar mixture of HFC-32 and HFC-134a, the model of Ref. [20] predicted the heat capacity with an average absolute deviation of 0.37 %. Since this is less than the experimental uncertainty of 0.7 %, it is clear that the model is successful at predicting thermodynamic properties of halocarbon mixtures.

3. Density

Densities of gaseous and liquid substances are essential physical properties for the design and development of industrial processes. Various methods exist for the accurate measurement of this property, including the Archimedes-type densimeter, Burnett method, isochoric method, and vibrating-tube densimeter.

3.1 Density Measurements of Pure Halogenated Hydrocarbons

The isochoric method was selected for this work due to its ruggedness, simplicity, and ease of automation. The original apparatus was built by Goodwin [3] for hydrogen studies, and was later modified and automated by Magee and Ely [21]. In this method, a sample of constant mass is confined in a thick-walled cell, while the temperature is precisely controlled and the pressure is accurately measured at equilibrium conditions. The sample mass is determined either by direct weighings or by a gas expansion into large calibrated volumes. Table 4 presents the ranges of conditions for our measurements of densities of pure halocarbons, and Table 5 presents the ranges of conditions for our reported saturated liquid densities for pure halocarbons.

3.2 Density Measurements of Mixed Halogenated Hydrocarbons

Densities of mixed halocarbons are seldom used directly to optimize the design of a refrigeration process, but rather are likely to be used to optimize a mixture model, such as the Helmholtz energy mixture model of Lemmon and Jacobsen. Table 6 presents the ranges studied for p-p-T measurements of mixtures containing halocarbons. Among the most thoroughly studied mixtures is the HFC-32 + HFC-134a system, for which we reported 461 measured densities. For this same binary mixture, the Lemmon and Jacobsen model [20] can calculate values of density that have an absolute average deviation from experimental results of 0.12 %, with a negligible bias of -0.01 %.

4. Vapor Pressure

An accurate knowledge of the vapor pressure is essential to the design of refrigeration processes. In a more fundamental sense, the vapor pressure as a function of temperature establishes the state conditions where gaseous and liquid states exist separately or may coexist.

The most accurate vapor pressures have been measured close to atmospheric pressure, with uncertainties approaching 1 part in 10^5 . However, vapor pressures measured at less than about 1 kPa often have unacceptably high uncertainty. The uncertainty of most experimental vapor pressures typically increases at lower pressures by about a power of 10 for every tenfold decrease in pressure. This implies that at 100 Pa, the possible uncertainty in a vapor pressure may approach 1 %. Practical needs exist for knowledge of vapor pressures that are considerably smaller than 100 Pa. For example, the vapor pressure of HFC-152a at the triple-point temperature is 64 Pa, and does not reach 10^5 Pa until the temperature is raised by 95 K; the pressure increases by 3 orders of magnitude over this temperature span. Improved experimental methods and tools to calculate reliable vapor pressures are necessary to fill this region.

One such method, presented by Weber [27], is an iterative technique for extrapolating vapor pressure data from atmospheric pressure to much lower temperatures by using measurements of saturated liquid heat capacity. Inspired by the observation mentioned in Section 3 that the linearity of our $C_v^{(2)}$ measurements provides direct information, from eq (2), on the second derivative of vapor pressure, Duarte-Garza and Magee [28] suggested a simple method that uses measurements of the internal energy change of a two-phase sample to establish the vapor pressure curve. This method applies eq (1) to calculate thermodynamically consistent vapor pressures from calorimetric data and a knowledge of the vapor pressure at a reference temperature. It exploits the linearity of two-phase internal energy versus specific volume and has the advantages of not using extrapolation or iteration to obtain the final results. Vapor pressures calculated in this way are not tainted by low-level volatile impurities that have been shown to cause substantial errors in measured vapor pressures. In this regard, Weber [29] used a mixture model to estimate that a minor air impurity, at a concentration of only 25 parts per million in HFC-134a, results in a measured vapor pressure that is 2.5 % too high at a temperature of 215 K, where the vapor pressure should be 18 kPa. Typically, the situation worsens at lower temperatures, particularly as the triple point temperature is approached. Table 7 presents vapor pressures for halocarbons. As denoted in the table, some of the vapor pressures were directly measured in our p-p-T apparatus, some were calculated with the iterative method of Weber, and some were calculated with the method of Duarte-Garza and Magee.

5. Impacts of this Program

Wide-ranging measurements of high-accuracy are often viewed as little more than scientific curiosities, until those measurements are applied to solving a significant problem. The thermodynamic measurements reviewed in Tables 1 through 7 played a key role in studies that were carried out under the auspices of Annex 18 of the IEA Heat Pump Programme, as described in detail by McLinden and Watanabe [1] in their final report. Annex 18 carried out evaluations of equations of state for HFC-134a, HCFC-123, HFC-32, HFC-125, and HFC-143a, and evaluated mixture models for mixtures containing HFC-32, HFC-125, and HFC-134a. For each pure substance, the Annex selected a formulation to give its formal endorsement and approval to appear in an issue of the *Journal of Physical and Chemical Reference Data*. In Table 3 of Ref. [1], McLinden and Watanabe listed the five formulations that were endorsed by Annex 18. While all three property types listed in Tables 1 through 7 were fitted to develop the properties formulations, there can be little doubt that heat capacity measurements had a significant impact. A good example of impact is refrigerant HFC-143a. The evaluators had more than 2800 p-p-T data at their disposal, most of which were recent and of high accuracy. All four competing property formulations represented these data roughly equivalently. As it turned out, heat capacities would separate two formulations from the pack. These two formulations showed superior representation of the measured liquid-phase heat capacities. In terms of average absolute deviations, the Li et al. formulation [32] gave an average absolute deviation of 0.36 %, and the formulation of Lemmon and Jacobsen [33] gave 0.18 %. While the Annex recognized these two formulations as essentially equivalent, the Lemmon and Jacobsen equation was selected as the international standard formulation. From a thermodynamic viewpoint, Lemmon and Jacobsen's liquid-phase calculations showed excellent consistency because their results agreed with vapor pressures [31] calculated from our calorimetric data, in a range of temperatures from the triple point to the normal boiling point. In this temperature range, the published directly-measured vapor pressure data are so inconsistent that they displayed three different trends with temperature, all of which were systematically higher than our calculated vapor pressures at temperatures below 225 K.

It is likely that working fluids used in future refrigeration cycles will be mixtures of two or more components. No matter how large an experimental effort might be made to measure the

needed properties of these mixtures, it would clearly be impossible to cover every conceivable mixture at every state condition. Therefore, it is clear that generalized wide-ranging theoretically based models must be developed to meet the need for reliable calculated thermodynamic properties. In support of generalized model development, we provided the measurements shown in Tables 3 and 6, representing more than 2000 state points. These data supported the development of Lemmon and Jacobsen's Helmholtz energy mixture model [20], which is currently the formulation employed in the widely used REFPROP database of the National Institute of Standards and Technology [34].

Annex 18 compared five thermodynamic property models for binary and ternary mixtures containing HFC-32, HFC-125, and HFC134a. The modelers compared their own models to a common database that included measurements from Tables 3 and 6. Annex 18 did not endorse one model over the others, but all the models proved to be very capable of representing mixture thermodynamic properties. The final comparisons were presented in a report by Lemmon [35].

6. Conclusions

The Experimental Properties of Fluids Group of the Physical and Chemical Properties Division at the National Institute of Standards and Technology in Boulder, Colorado has developed experimental apparatus and computational tools to establish accurate data for the heat capacity, density, and vapor pressure of refrigerants. While an earlier paper reviewed our studies on natural refrigerants [36], this paper reviewed a total of over 6000 published data points for halogenated hydrocarbons. Because many potential refrigerants are mixtures, NIST has also developed capabilities for preparing and handling these mixtures. In order to support the development of reliable models for thermodynamic properties, it will be necessary to continue this research program into new areas that fill gaps in the database, requiring a close collaboration between experimental and modeling efforts.

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Table 1. Ranges of temperatures, pressures, and number N of data for heat capacity C_v measurements on halocarbons at NIST.

Substance	T / K		P / MPa		N	Ref.
HFC-134a	186.8	343.3	2.58	34.89	150	9
HFC-32	152.9	341.2	5.24	31.75	73	12
HFC-125	200.2	322.2	3.79	33.26	99	12
HFC-41	148.4	342.7	3.23	33.02	122	13
HFC-152a	164.2	342.9	3.03	34.02	85	14
HFC-143a	172.6	342.1	3.14	34.31	136	14
HCFC-123	195.6	341.4	2.72	31.60	79	15
HCFC-124	116.6	340.8	2.32	33.58	82	15
HCFC-13	99.8	338.5	1.75	33.37	101	16
HFC-23	125.0	341.9	5.69	33.53	111	17
					Total 1038	

Table 2. Ranges of temperatures, pressures, and number N of data for saturated liquid heat capacity C_p measurements on halocarbons at NIST.

Substance	T/K		P/kPa	N	Ref.	
HFC-134a	172.0	289.9	0.1	515	160	9
HFC-32	141.2	342.2	0.1	4776	101	12
HFC-125	175.9	278.0	4	778	93	12
HFC-41	134.1	314.4	1	5537	133	13
HFC-152a	162.6	314.9	0.2	952	66	14
HFC-143a	164.8	343.4	1.5	3573	80	14
HCFC-123	166.9	304.1	0.01	113	88	15
HCFC-124	94.3	317.8	0.01	674	117	15
HFC-23	120.6	295.1	0.1	4348	94	17
					—	
Total					932	

Table 3. Mole fraction compositions and ranges of temperatures, pressures, and number N of data for heat capacity C_v measurements on halocarbon mixtures at NIST.

Designation	Comp. 1	Mole Fraction Comp. 2	Comp. 3	T/K	P/MPa	N	Ref.
DOE1	HFC-32 0.4997	HFC-134a 0.5003		205.2 342.6	4.32 33.50	131	18
DOE2	HFC-32 0.4996	HFC-125 0.5004		207.6 344.6	4.31 33.32	111	18
DOE4	HFC-125 0.5001	HFC-134a 0.4999		206.3 343.4	3.83 31.64	94	18
ART1 1	HFC-125 0.5000	HFC-143a 0.5000		205.3 343.7	4.51 32.71	109	18
DOE17	HFC-32 0.3337	HFC-125 0.3333	HFC-134a 0.3330	203.6 344.6	4.23 32.63	64	19
DOE18	0.3808	0.1798	0.4394	202.7 342.4	4.26 33.39	68	19
Total 577							

Table 4. Ranges of temperatures, pressures, densities, and number N of data for p- ρ -T measurements on halocarbons at NIST.

Substance	T/K		P/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$		N	Ref.	
HFC-134a	173	400	1.72	35.08	87.59	1585.9	241	22
HFC-32	142	396	3.82	35.08	708.0	1419.5	136	23
HFC-125	178	398	3.58	35.40	1114.6	1683.7	77	23
HFC-41	132	400	2.99	35.40	46.80	1007.7	445	13
HFC-152a	158	400	2.05	35.19	638.9	1188.0	134	24
HFC-143a	166	400	3.04	35.12	715.4	1323.8	144	24
HCFC-123	176	380	0.841	34.55	1376.9	1751.7	104	25
HCFC-124	104	400	1.22	35.47	1126.5	1899.5	149	25
HCFC-13	94	350	0.772	35.43	208.3	1869.3	106	16
Total							1536	

Table 5. Range of temperatures and number N of data for saturated liquid densities of halocarbons at NIST.

Substance	T/K		N	Ref.
HFC-134a	172.0	358.9	11	22
HFC-32	138.9	304.7	13	23
HFC-125	173.5	308.5	7	23
HFC-41	130.8	309.0	13	13
HFC-152a	157.0	318.5	9	24
HFC-143a	164.1	298.0	8	24
HCFC-123	174.0	328.4	8	25
HCFC-124	102.1	352.5	14	25
			—	
			Total	83

Table 6. Mole fractions and ranges of temperature, pressure, density, and number N of data for p-p-T measurements on halocarbon mixtures at NIST.

Designation	Comp. 1	Mole Fraction Comp. 2	Comp. 3	T/K	P/MPa	$\rho/\text{mol}\cdot\text{L}^{-1}$	N	Ref.
DOE1	HFC-32 0.4997	HFC-134a 0.5003		200 400	2.70 35.45	1.101 18.47	219	26
DOE2	HFC-32 0.4996	HFC-125 0.5004		200 400	2.57 35.34	1.062 17.35	228	26
DOE3	HFC-32 0.3288	HFC-134a 0.6712		200 400	2.70 35.45	1.123 17.00	242	26
DOE4	HFC-125 0.5001	HFC-134a 0.4999		200 400	3.15 35.45	1.664 14.11	268	26
ARTI 1	HFC-125 0.5000	HFC-143a 0.5000		200 400	2.13 35.41	0.881 14.08	281	26
DOE17	HFC-32 0.3337	HFC-125 0.3333	HFC-134a 0.3330	200 400	3.25 35.17	1.577 16.44	181	19
DOE18	03808	0.1798	0.4394	200 400	2.97 34.30	1.668 17.09	171	19
ARTI 2	HFC-41 0.4998	CO ₂ 0.5002		192 400	3.64 35.48	1.708 27.58	214	13
Total							1804	

Table 7. Ranges of temperatures, pressures, and number N of data for vapor pressures of halocarbons that are directly measured, calculated from saturated liquid heat capacity C_o and calculated from two-phase internal energy increments $U^{(2)}$ at NIST.

Substance	Method	T/K		P/kPa		N	Ref.
HFC-134a	direct	180	350	1.152	2460.5	19	30
HFC-32	direct	270	330	733.8	3665.6	7	23
HFC-32	C_o	140	180	0.081	6.798	9	12
HFC-125	direct	180	335	5.76	3297.6	33	23
HFC-125	C_o	170	250	2.333	299.19	9	12
HFC-41	direct	170	317	20.65	5861.7	31	13
HFC-134a	$U^{(2)}$	169.85	250	0.390	115.56	18	28
HFC-32	$U^{(2)}$	136.34	220	0.046	93.816	18	28
HFC-125	$U^{(2)}$	172.52	225	2.916	101.04	12	28
HFC-41	$U^{(2)}$	129.82	250	0.322	1030.15	26	31
HFC-143a	$U^{(2)}$	161.34	230	1.077	122.48	15	31
HFC-152a	$U^{(2)}$	154.56	250	0.064	105.29	21	31
HFC-152a	C_o	170	250	0.415	105.28	9	14
HFC-143a	C_o	165	225	1.560	96.816	13	14
HCFC-13	direct	250	302	1036.6	3875.8	13	16
HCFC-123	C_o	170	250	0.0074	10.08	9	15
HCFC-124	C_o	140	260	0.002	96.25	13	15
HFC-23	$U^{(2)}$	118.02	190	0.058	94.86	<u>73</u>	17
Total 348							

